Study of Dry Etching Resistance of Methacrylate Polymers for ArF Excimer Laser Lithography

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ABSTRACT

We have investigated dry-etching resistance of methacrylate polymers for use as ArF chemically amplified resists and proposed a new etching model that can predict the etching rate very accurately. The examined polymers were methacrylate polymers with alicyclic groups. The polymers were dry etched using a LAM TCP-9400 machine under the chlorine-based gas conditions used for poly-silicon etching. The obtained etching rate was explained in term of a carbon-atom-density parameter known as the ohnishi parameter. However, the fitting accuracy is not good enough especially for alicyclic polymers (R=0.87). And a ring parameter model also resulted in a similar fitting accuracy (R=0.86). Hence, we proposed a new model that introduced polymer-structure dependence into the carbon-atom-density model. The new model gives excellent agreement with measured data (R=0.99). And it is very useful in designing ArF resist polymers and predicting etching resistance of future ArF resists.

Keywords: polymer, alicyclic, ArF, dry etching, resist, methacrylate

1. INTRODUCTION

ArF excimer laser lithography is expected to become the technique for fabricating small feature sizes less than 0.15 μm. Instead of conventional novolac or polyhydroxylene polymers, many kinds of methacrylate polymers that include alicyclic groups have been proposed for ArF lithography.[1-5] Here, one of the important issues concerning ArF resists is the dry-etching resistance. It is known that most methacrylate polymers proposed for ArF resists have less dry-etching resistance than conventional novolac resists. For predicting the dry-etching resistance of organic polymers, the carbon-atom-density model (Ohnishi parameter) is used.[6-7] This model can predict polymer dry-etching resistance, so it is very useful in designing ArF resist polymers. However, the model has a non-negligible error depending on the polymer and etching conditions. Although another etching model was proposed to improve prediction accuracy, prediction accuracy was still large.

Hence, we proposed a new model which introduced polymer structure dependence into the carbon-atom-density model. The new model gives excellent agreement with measured data (R=0.99). And it is very useful for designing ArF resist polymers and predicting future ArF resist performance.

2. EXPERIMENTAL

The examined polymers were methacrylate polymers with alicyclic groups, methacrylate polymers with alicyclic groups in main the chain, and conventional novolac, poly-hydroxystylene polymers as references. The chemical structures of these polymers are shown in Fig. 1.

The polymers were dissolved into appropriate solvents such as propylene glycol methyl ether acetate (PGMEA) and Ethyl lactate (EL) with about 15 wt%. The solution was spun onto silicon wafers and baked at 120℃ for 60 seconds. The initial thickness was about 0.7 μm. We used a TCP-9400 etching machine of LAM research with the Cl/HBr gasses listed in Table 1. The etching rate was derived from the reduction in resist thickness during etching. The resist thickness was monitored with an optical monitor from Zeiss.

0277-786X/98/$10.00

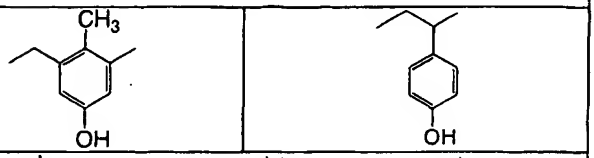
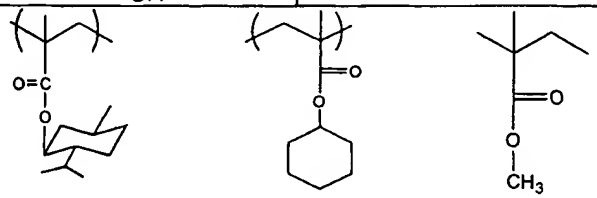
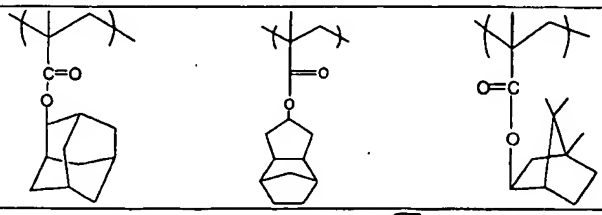
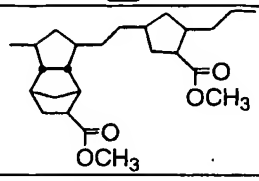
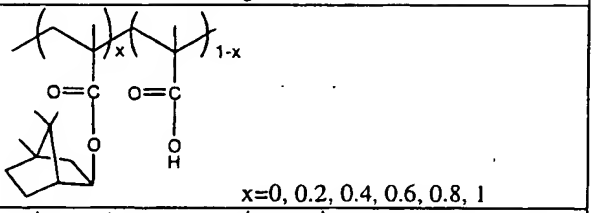
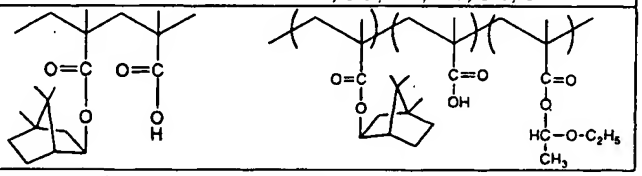
		Structure	Chemical structure
Aromatic	Conventional Polymer	Mono-cyclic Main-chain Side-chain	
Alicyclic	Homo-polymer	Non-, mono-cyclic Side-chain structure	
		Multi-cyclic Side-chain	
		Multi and monocyclic Main-chain	
	Co-polymer	Multi-cyclic Main-chain	 x=0, 0.2, 0.4, 0.6, 0.8, 1
	ArF resist polymer	Partially protected	

Fig. 1 Chemical structure of the investigated polymers

Table 1 Dry etching conditions

Etching equipment	TCP-9400 (LAM)
Gas	Cl_2 / O_2 / HBr (sccm)
Temperature	75℃
Pressure	5 (mTorr)
Time	60 s

3. RESULTS

Figure 2 shows the measured etching rate as a function of the density of effective carbon atoms. This density was calculated from $N_T/(N_C-N_O)$. Here, N_T is the total number of all atoms, N_C is the number of carbon atoms, and N_O is the number of oxygen atoms. This carbon atom density is known as the Ohnishi parameter.[6-7] According to the Ohnishi model, the etching rate is proportional to this parameter as follows.

$$Etching\ Rate \propto \frac{N_T}{(N_C - N_O)} \tag{1}$$

Figure 2 indicates that the measured etching rate is roughly proportional to the carbon atom density. The correlation factor of this approximation is 0.87. This approximation error ($\pm 20\%$) is too large for a prediction model of etching rate.

An alternative etching rate model is the ring-parameter model proposed by Kunz.[8] In this model, the etching rate is thought to be proportional to a ring parameter defined as follows.

$$Etching\ Rate \propto \frac{M_{CR}}{M_{TOT}} \tag{2}$$

Where, M_{CR} indicates the mass of carbon atoms contained in a ring and M_{TOT} represents the total mass of the resist. Figure 3 shows the measured etching rate as a function of the ring parameter. The prediction accuracy is not improved at all (as the correlation factor of 0.86 indicates). The biggest problem with the model based on the ring parameter is that it cannot explain the difference in etching resistance of the polymers which do not include a ring structure (such as poly-methylmethacrylate (PMMA) and acrylonitrile terpolymer (AN-MAA-MMA)).

The conventional etching rate models are clearly not accurate enough. Next, we analyze the obtained etching rates carefully in order to construct a more accurate model. We found that alicyclic methacrylates, which have multi-cyclic groups, had smaller etching rates than expected. Hence we divided the polymers with different etching rates into two groups depending on their chemical structures (Fig. 4). This figure clearly shows that etching rate depends on chemical structure. The etching rate of methacrylate polymers with monocyclic or non-cyclic groups is proportional to carbon atom density, and the proportional coefficient is 0.42. Although the etching rates of methacrylate polymers with multi-cyclic groups as a side chain were also proportional to carbon density, the coefficient is smaller than that for monocyclic methacrylate. If we use two coefficients for predicting the etching rate, all the points are on the predicted lines. Although the novolac resist has monocyclic groups, the obtained etching rate well agrees with the rate for multi-cyclic polymers. This is because the novolac polymer has a ring in the main chain so it has higher etching resistance.

Based on this analysis, we propose a new model for predicting etching rate as follows.

$$Etching\ Rate = K_S \frac{N_T}{(N_C - N_O)} \tag{3}$$

In addition to carbon atom density, we introduced a coefficient of structure dependence K_S. And K_S is 0.42 for mono-cyclic polymers and 0.29 for multi-cyclic polymers. Here, the etching rate is normalized to poly-hydroxystylene polymer. Figure 5 indicates the relationship between the measured and the predicted etching rates. This new model can accurately predict measured etching rate as shown in Figure 5. The correlation factor of 0.99 is exccelent. This new etching rate model is very useful in designing new polymers. And its validity was proved for homo-polymer.

Next, we analyzed the co-polymer etching rate. Figure 6 shows measured etching rate of isobornylmethacrylate-methacrylicacid co-polymers ($IBMA_x$-MAA_{1-x}). The IBMA content (x) of the co-polymers was varied from 0 to 1. As mentioned previously, the etching rate coefficients of non-cyclic polymers and multi-cyclic polymers are different. Therefore, the etching rate coefficient of an IBMA-MAA co-polymer consisting of both non-cyclic polymer and multi-cyclic

polymer is unknown. We speculate that the etching rate coefficient of these co-polymers is between that of the non-cyclic polymer coefficient (0.42) and that of the multi-cyclic polymer coefficient (0.29). As shown in Figure 6, the measured co-polymer (IBMAx-MAA1-x) etching rate is on the line that connects the MAA and IBMA rates. This means that our new model, which consideres structure dependence in the etching rate model, is also applicable to co-polymers. The values of K_S are summarized in Table 2.

Table 2 Obtained coefficient values K_S

	Structure type	Cyclic type	K_S
Aromatic polymer	Side-chain	Mono	0.42
	Main chain	Mono	0.29
Alicyclic polymer	Side-chain	Non-, mono	0.42
	Side-chain	Multi	0.29
	Main chain	Multi	
	Side-chain	Mono and Multi	0.29-0.42
	Side-chain	Non-, Multi-cyclic partially protected	0.29-0.42<

Next, we applied our new model to ArF resists consisting of partially protected methacrylate ter-polymer and photoacid generator (PAG). The ter-polymer consists of isobornylmethacrylate-protected methacrylate-methacrylic acid (IBMA-RMA-MAA). Figure 7 shows the measured etching rates of ArF resists. We expected the etching rates of these resists to be similar to the etching rate characteristics of the co-polymers. However, the measured etching rates are generally larger than those of the co-polymers. The reason for this increased etching rate is that the protected groups of resist polymers become unprotected during dry etching due to exposure to thermal energy and plasma light. The deprotected resist polymer has therefore higher methacrylic-acid content and this results in lower dry-etching resistance.

4. CONCLUSION

We have investigated the dry etching resistance of alicyclic polymers used for the ArF lithography. Since the conventional etching rate model has a non-negligible error, we proposed a new prediction model that considers the chemical structure of the polymers. The new model has an excellent prediction accuracy. And it is very useful in designing new resist polymers with a high etching resistance.

5. ACKNOWLEGEMENTS

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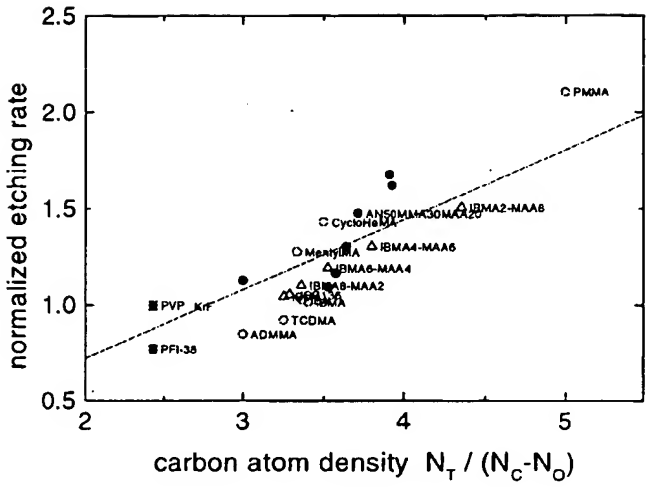

Figure 2 Measured polymer dry etching resistance as a function of carbon atomic density (R=0.87). This density is known as the Ohnishi parameter.

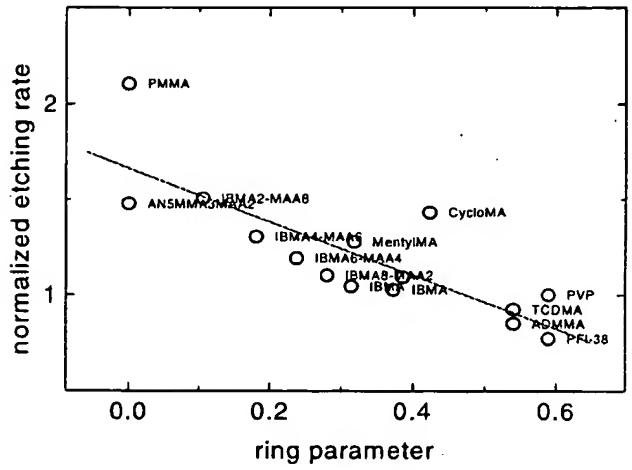

Figure 3 Measured polymer etching rate as a function of ring parameter.

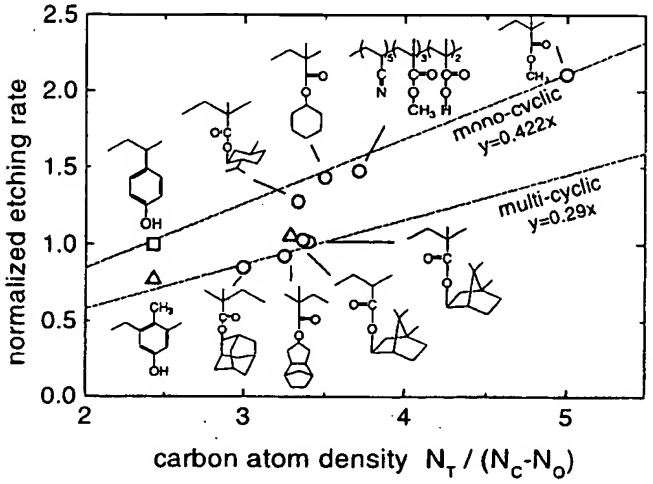

Figure 4 The relationship between normalized dry etching rates and carbon atom density for homopolymers with different chemical structures. The dry etching rate of homopolymer can be divided into two groups depending on the structure.

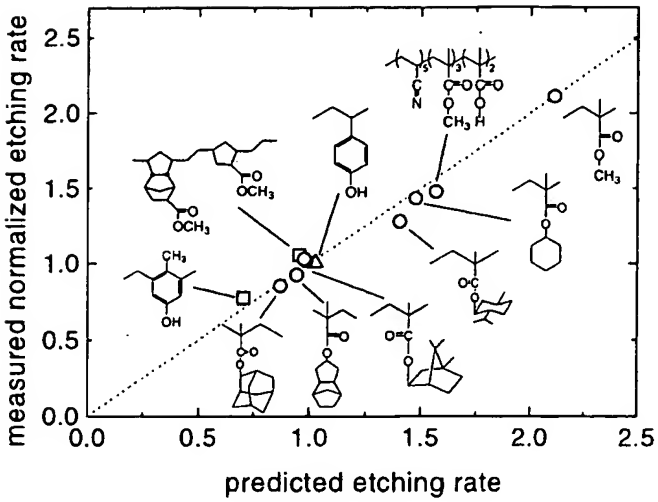

Figure 5 Prediction accuracy of new etching model. The new model can predict the rate for all kinds of homopolymers (R=0.99).

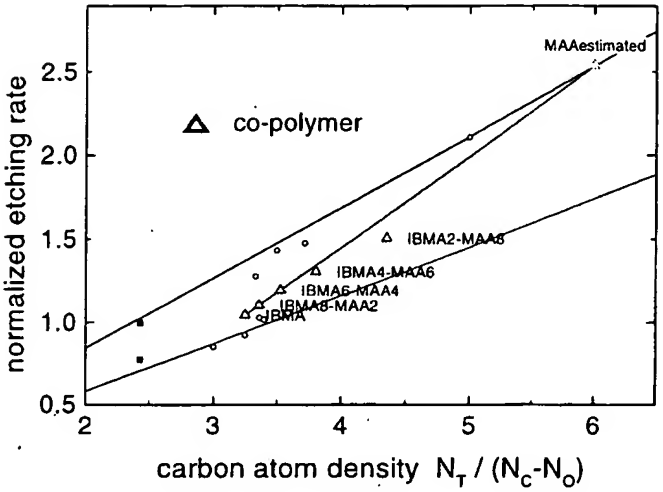

Figure 6 Measured dry etching rate of co-polymer ($IBMA_x$-MAA_{1-x}). The co-polymer etching rate is also predictable.

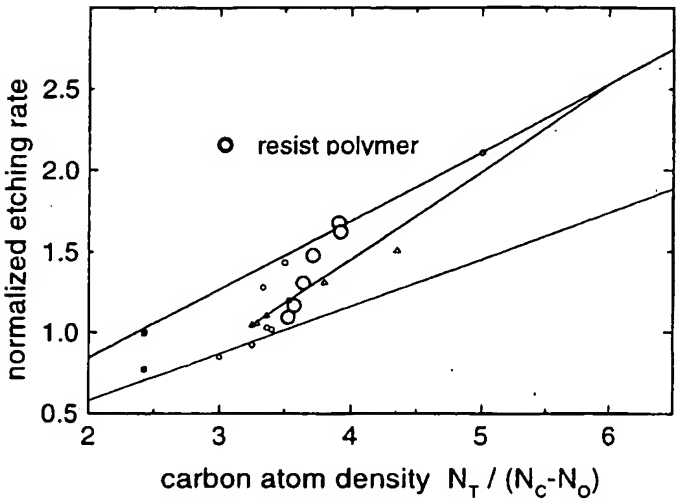

Figure 7 Measured etching rate of ArF resist polymer. The resist polymers have higher etching rate than those expected because of deprotection reaction during etching.